III.A.18 Low-Cost Integrated Composite Seal for SOFC: Materials and Design Methodologies

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Objectives

- Prove a novel layered composite seal concept (materials and structures) for solid oxide fuel cells (SOFCs).
- Characterize the sealing and the mechanical performance of the layered composite seal and demonstrate a design methodology.

Approach

- Down-select a set of constituent materials and fabricate small-scale composite seal samples (button samples) for material characterization and seal testing.
- Test button samples for seal performance, mechanical strength, long-term material stability and compatibility.
- Analyze failed samples and determine failure modes and mechanisms; model stress and strain in the seal structure.

Accomplishments

- Completed design, assembly, and qualification of an automated SOFC seal leak testing stand.
- Developed a robust alumina-zirconia composite coating on Fe-Cr based metallic substrates using low-cost ceramic powders; fabricated sub-scale composite seal button samples infiltrated with various glass-based fillers.
- Demonstrated thermo-cycle resistance from 800ºC to 150ºC with a heating and cooling rate of 5ºC/min. After 40 cycles, leak rates of less than 0.017 sccm/cm were found, and after 80 cycles, leak rates of less than 3.1 sccm/cm were found. (Leak rate was measured with helium at 2 psid at 800ºC.)
- Observed healing behavior of the composite seal when using a low-softening point filler glass. The leak rate of the sample with cracked filler glass was restored to the level before cracking by heating the composite seal above the softening temperature of the filler glass.

Future Directions

- Continue with leakage testing to determine leak rates as a function of thermo-cycling and aging time; perform root cause analysis by analyzing failed seal samples.
- Evaluate additional filler materials in composite seal configuration.

- Perform long-term material compatibility studies and characterize failed samples for morphological change and chemical interactions.
- Perform mechanical testing and complete modeling efforts.

Introduction

Maintaining stable hermetic sealing is critical for SOFC stacks to achieve high efficiency and longevity. Sealing SOFC stacks is a challenging task for many reasons. The adherents to be sealed often have very different thermo-elastic properties; the temperature field in SOFC stacks is typically non-uniform, particularly in transient conditions, such as during start-up and shut-down. As a result, large thermal stresses can be induced in the seals and the adjacent components if rigidly bonded. Commonly used glass seals and the materials in a SOFC cell assembly to be jointed or sealed are brittle. Existing glass and glass ceramic seals have shown poor resistance to mechanical failure during thermo-cycling, among other operating conditions. In the long term, sealing glass reacts with Fe-Cr based interconnect material, resulting in a weakened interface [1]. Compressive mica and mica composite seals [2] have been shown to have excellent thermo-cycling stability. However, they require expansive high-temperature load-frame to maintain a high compressive force.

SOFC sealing material is subjected to a complex set of requirements, including good wetability to adherends, good chemical compatibility, good match of thermal expansion coefficients, high electrical resistivity, etc. In addition, the aggregated material and fabrication cost of seals has to be low to ensure commercial viability. It is unlikely that such a large set of suitable mechanical/physical/chemical properties occur in one material. Attempting to break the current technical barriers related to SOFC seals, the authors are investigating a novel integrated composite seal concept (materials and structures) and its associated thermal mechanical design methodologies.

Approach

The approach being pursued is to engineer composites of multiple constituent materials or ingredients. The authors are investigating a multi-layered composite seal structure (Figure 1) that consists of thin layers of oxidation-resistant metals, porous ceramics, and fillers/glasses. The seal structure will be directly fabricated onto the surfaces of mating adherends using low-cost manufacturing methods such as atmospheric plasma spray (APS). During stack assembly, sealing can be achieved through a simple heat/pressure-assisted curing process. As such, stack cost can potentially be lowered by reducing the total number of parts and by simplifying the assembly process. Properly designed multi-layered composite structure enables a gradual transition of thermo-elastic properties from the substrate to the glass fillers, alleviating stress concentrations. Plasma-sprayed ceramic layers can form strong bonds with properly prepared metal substrate. The ceramic layer is electrically insulating and has shown very good thermal shock resistance. Filling in the pores and gaps between the ceramic layers, a thin layer of glass joins the adherends together and forms a hermetic seal. Because of the excellent refractory properties of the coating, the requirements (wetting, dielectric, chemical properties, etc.) on the filler materials can be relaxed; hence, many types of filler materials can be utilized in the composite seal structure. Eliminating direct contact between the glass and the alloy, the composite seal will also have improved long-term stability.

Small-scale sealed specimens will be subjected to thermo-cycles and sustained loading similar to fuel cell operating conditions in air. Post-mortem

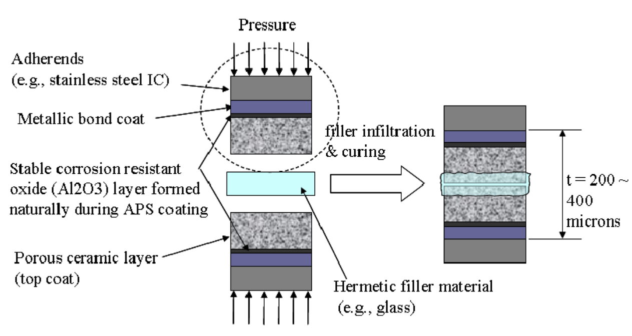

Figure 1. Concept of an Integrated Composite Seal for SOFC Stacks Being Developed at the University of Connecticut

analysis will be conducted to investigate interfacial failure modes and failure mechanisms. These activities will be iterated for different combinations of material compositions in order to achieve high interfacial bond strength and good sealing performance. To demonstrate the above composite seal concept, the authors are following an iterative process including material selection, fabrication, screening, seal performance evaluation, and mechanical performance evaluation.

Results

As part of the layered composite seal, a porous alumina-YSZ (yttria-stabilized zirconia) ceramic coating on Fe-Cr based interconnect material has been developed. The coating was made from low-cost commercially available powders and deposited by atmospheric plasma spray method. The coating composition was optimized for high mechanical strength/toughness, low electric conductivity, and good refractory properties. The coating has demonstrated superior high-temperature stability, high electrical resistivity and superior thermal shock resistance (survived repeated water quench from 850ºC). The projected cost for material and fabrication of the coating is less than $1 per square inch coated area. The microstructure of the coating was characterized by optical and scanning electron microcopy. The bulk of the coating consists of flattened "splats" with inter- and intra- splat micro-cracks. The porosity of the coating was revealed to be greater than 15%, as determined by mercury intrusion porosimetry.

To facilitate sealing performance measurements, an automated SOFC seal leak test stand was developed and qualified. The test stand consists of a pneumatic loading module for maintaining a constant compressive load, a heating and temperature control module, and a leak rate testing module to measure the flow rate of test media. SOFC seal samples up to 5 inches in diameter can be placed in the heated chamber and maintained at temperature anywhere from room temperature to 1100ºC. The temperature can also be cycled repeatedly with controlled heating and cooling rates. The leak rate in the range from 0.1 to 125 sccm can be continuously monitored.

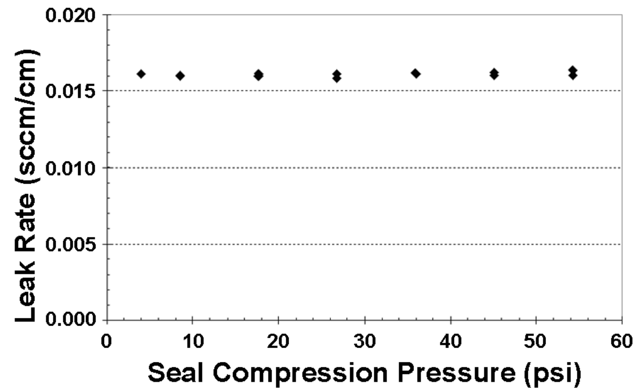

Figure 2. Measured composite seal leak rate as a function of the applied compressive pressure on the substrates. The composite seal leak rates are shown to be independent of the compression force.

Composite seal samples have been made using commercial glasses as well as glasses provided by several Solid State Energy Conversion Alliance (SECA) peers (Richard Brow, University of Missouri-Rolla; Raj Singh, University of Cincinnati; Ron Loehman, Sandia National Laboratories). The filler glass was infiltrated into the porous ceramic coating, and interconnect-to-interconnect and interconnect-to-electrolyte seal samples have been made and tested. At steady state, a typical leak rate of 0.016 sccm/cm (helium at 2 psid) was found. As shown in Figure 2, it was discovered that the leak rate of the composite seal is independent of the compressive force exerted on the sealed substrate. It was found that the leak rate is proportional to the differential pressure of the test media. The measured leak rate of a sample as a function of differential pressure is shown in Figure 3. Such behavior allows us to reliably predict leak rate at lower differential pressure using leak rate measured at higher differential pressure.

Thermo-cycle testing has been conducted with a 1.5" diameter interconnect-to-interconnect seal sample. The temperature was programmed to cycle between 800ºC and 150ºC using a ramp rate of approximately 5ºC/min. The sealed chamber was filled with pure helium gas and maintained at about 2 psig. After more than 40 cycles, leak rates of less than 0.017 sccm/cm were found; after 80 cycles, leak rates of less than 3.1 sccm/cm were found. Figure 4 shows the data recorded near the end of an 80-cycle

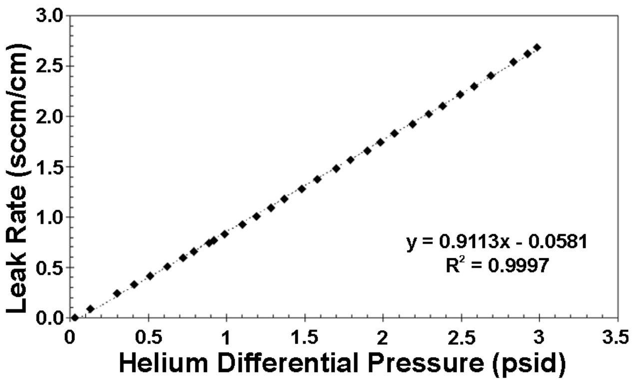

Figure 3. Measured leak rate as a function of differential pressure of helium gas that was used as the test media. The leak rate is shown to be proportional to applied differential pressure.

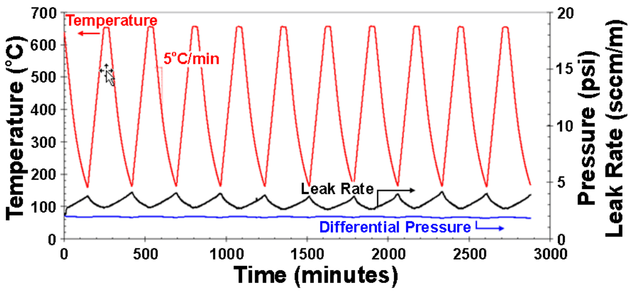

Figure 4. Thermal Cycling Performance of a Composite Seal near the End of an 80-Cycle Test

test. It was also observed that a "failed" composite seal with cracked filler glasses with a low softening point can be "healed" multiple times. The "healing" involves heating the seal to about the softening point of the filler (typically 800ºC) and dwelling for one hour.

Conclusions

In the first year of the program, the University of Connecticut team has made significant progress on proving the novel composite seal concept. A streamlined procedure has been established, from material selection and seal sample fabrication, to material characterization and seal performance testing under relevant conditions. The layered composite seal has shown good steady-state sealing performance and reasonable thermo-cycle resistance. Future work will focus on proving the durability of the composite seal, further improving the thermal cycle resistance, and establishing the mechanical testing, modeling and design approaches.

FY 2005 Publications/Presentations

1. "Low-Cost Integrated Composite Seal for SOFC: Materials and Design Methodologies," X. Huang, K. Ridgeway, S. Narasimhan, Y. Du, K. Reifsnider, C. Ma, F. Shu, Presented at the Sixth Annual SECA Workshop, Asilomar, CA, April 18-21, 2005.

References

1. Z. Yang, J.W. Stevenson, K.D. Meinhardt, "Chemical interactions of barium-calcium-aluminosilicate-based sealing glasses with oxidation resistant alloys," Solid State Ionics, 160 (2003), 213~225.
2. S.P. Simner, J.W. Stevenson, "Compressive mica seals for SOFC applications," J. of Power Sources 102 (2001), 310~316.